Where the level of potentially interfering compounds is relatively low and not rapidly changing, the previous system has operated successfully using the sample gas with the H_2S selectively removed as the "zero" reference gas. Potentially interfering compounds are those with conjugated double bonds, such as 1,3-butadiene and aromatics and other sulfur compounds.

Where background absorbance is excessively high and changing rapidly, a special system has been developed for selective H_2S analysis. In this system, H_2S is extracted with a dilute ammonium hydroxide solution, and the strong UV absorption of the ammonium sulfide formed in solution is measured and calibrated for H_2S concentration in the gas stream.

Chromatograph

Process gas chromatographs have been designed for environmental monitoring of H_2S at the ppm level using the sulfur-specific flame photometric detector (FPD) (Figure 1.31g). See Chapter 227 for the basic principles of gas chromatography and a more detailed description of the FPD.

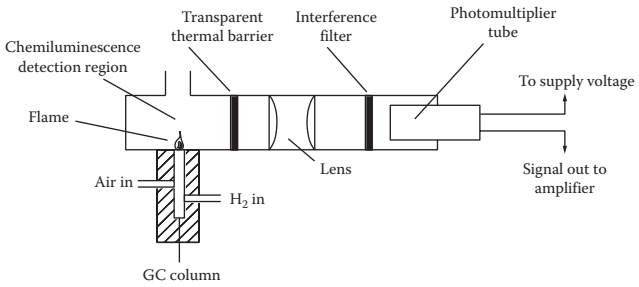

FIG. 1.31g
The flame photometric detector.

APPLICATIONS

For Claus sulfur recovery applications, a top of the pipe analyzer is available, which can measure both H_2S and SO_2. An installed unit is shown in Figure 1.31h.

FIG. 1.31h
Top of the pipe tail gas analyzer detects both H_2S and SO_2. (Courtesy of Ametek Process Instruments.)

SPECIFICATION FORMS

When specifying hydrogen sulfide analyzers only, one can use the ISA form 20A1001, and when specifying both the analyzer and the composition or properties of the process, which it will be monitoring, use the ISA form 20A1002. Both forms are reproduced with the permission of the International Society of Automation on the next pages.

1		RESPONSIBLE ORGANIZATION		ANALYSIS DEVICE		6		SPECIFICATION IDENTIFICATIONS	
2						7		Document no	
3				Operating Parameters		8		Latest revision	Date
4						9		Issue status	
5						10			

11		ADMINISTRATIVE IDENTIFICATIONS				40		SERVICE IDENTIFICATIONS Continued			
12		Project number		Sub project no		41		Return conn matl type			
13		Project				42		Inline hazardous area cl		Div/Zon	Group
14		Enterprise				43		Inline area min ign temp		Temp ident number	
15		Site				44		Remote hazardous area cl		Div/Zon	Group
16		Area	Cell	Unit		45		Remote area min ign temp		Temp ident number	
17						46					
18		SERVICE IDENTIFICATIONS				47					
19		Tag no/Functional ident				48		COMPONENT DESIGN CRITERIA			
20		Related equipment				49		Component type			
21		Service				50		Component style			
22						51		Output signal type			
23		P&ID/Reference dwg				52		Characteristic curve			
24		Process line/nozzle no				53		Compensation style			
25		Process conn pipe spec				54		Type of protection			
26		Process conn nominal size		Rating		55		Criticality code			
27		Process conn termn type		Style		56		Max EMI susceptibility		Ref	
28		Process conn schedule no	Wall thickness			57		Max temperature effect		Ref	
29		Process connection length				58		Max sample time lag			
30		Process line matl type				59		Max response time			
31		Fast loop line number				60		Min required accuracy		Ref	
32		Fast loop pipe spec				61		Avail nom power supply		Number wires	
33		Fast loop conn nom size		Rating		62		Calibration method			
34		Fast loop conn termn type		Style		63		Testing/Listing agency			
35		Fast loop schedule no	Wall thickness			64		Test requirements			
36		Fast loop estimated lg				65		Supply loss failure mode			
37		Fast loop material type				66		Signal loss failure mode			
38		Return conn nominal size		Rating		67					
39		Return conn termn type		Style		68					

69		PROCESS VARIABLES	MATERIAL FLOW CONDITIONS				101		PROCESS DESIGN CONDITIONS		
70		Flow Case Identification				Units	102		Minimum	Maximum	Units
71		Process pressure					103				
72		Process temperature					104				
73		Process phase type					105				
74		Process liquid actl flow					106				
75		Process vapor actl flow					107				
76		Process vapor std flow					108				
77		Process liquid density					109				
78		Process vapor density					110				
79		Process liquid viscosity					111				
80		Sample return pressure					112				
81		Sample vent/drain press					113				
82		Sample temperature					114				
83		Sample phase type					115				
84		Fast loop liq actl flow					116				
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88		Conductivity/Resistivity					120				
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97		Sample lag time					129				
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133		MATERIAL PROPERTIES				137		MATERIAL PROPERTIES Continued			
134		Name				138		NFPA health hazard		Flammability	Reactivity
135		Density at ref temp		At		139					
136						140					

Rev	Date	Revision Description	By	Appv1	Appv2	Appv3	REMARKS

Form: 20A1001 Rev 0

RESPONSIBLE ORGANIZATION	ANALYSIS DEVICE COMPOSITION OR PROPERTY Operating Parameters (Continued)	SPECIFICATION IDENTIFICATIONS
		Document no
		Latest revision / Date
		Issue status

PROCESS COMPOSITION OR PROPERTY			MEASUREMENT DESIGN CONDITIONS				
Component/Property Name	Normal	Units	Minimum	Units	Maximum	Units	Repeatability

Rev	Date	Revision Description	By	Appv1	Appv2	Appv3	REMARKS

Form: 20A1002 Rev 0

Abbreviations

FPD	Flame photometric detector
LED	Light emitting diode
MOS	Metal oxide semiconductor
UV	Ultraviolet

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EPA, Acute exposure guideline levels for airborne chemicals, (2015) http://www.epa.gov/oppt/aegl/index.htm.

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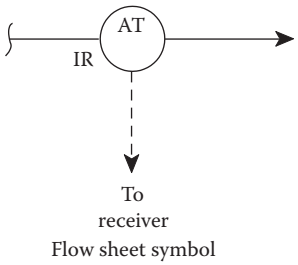
1.32 Infrared and Near-Infrared Analyzers

J. E. BROWN (1969) **A. C. GILBY** (1982)
B. G. LIPTÁK and T. M. CARDIS (1995)
E. H. BAUGHMAN (2003) **B. G. LIPTÁK** (2017)



Flow sheet symbol

INFRARED ANALYZERS

Process streams	Gas or liquid, surface analysis of solids
Ranges and applications (See Table 1.32a)	Maximum range is usually 100%, with path length adjustment Ammonia—100 ppm Carbon monoxide—25 ppm Carbon dioxide—20 ppm Ethylene—100 ppm Hexane—100 ppm Methane—10 ppm Moisture (humidity)—50 ppm Nitrous oxide—10 ppm Propane—100 ppm Sulfur dioxide—100 ppm (*Notes:* 1. Some of these analytes can be measured by UV (Chapter 1.69), for example, sulfur dioxide. 2. The minimum range is also a function of the matrix—the minimum for benzene in air is going to be much lower than that for benzene in gasoline. 3. The normal range is a factor of 10, so ammonia could be 10–100 ppm or 1%–10%, but not 100 ppm to 10%. 4. These are examples only, not an exclusive list.)
Operating pressure	Standard from atmospheric to 150 psig (10 bars); special up to 1000 psig (70 bars)
Operating Temperature	–40°C to 50°C (–40°F to 120°F) is standard; probe temperatures can be higher with special Arrangements
Humidity limitations	Up to 95% relative humidity (normally the instrument is purged, which negates the effect of humidity in the atmosphere).
Materials of construction	Cell bodies are available in all standard materials; windows can be made of sodium chloride, calcium fluoride, barium fluoride, sapphire, or zinc selenide
Cell lengths	For liquids, from 0.004 to 4 in. (0.1 to 100 mm); for gases, up to 40 m (130 ft) enclosed and any length for open-path monitoring
Warm-up time	15–20 min. (For most stable operation, allow 16 hr for warm-up.)
Repeatability	±1% of full scale
Linearity	±0.5 of full scale
Inaccuracy	±2% of span
Drift	±1% of full scale for zero and the same for span per day

(*Continued*)

Costs

Remember that the installation and upkeep costs are normally much larger than just the vendor costs given below.
Single-beam portable or laboratory units cost $4000–$5000
Industrial nondispersive infrared analyzer with diaphragm capacitor costs $8,000
Multigas analyzer pulling in up to five gases from 50-m (150-ft) distances costs $25,000–$27,000
Microprocessor-based portable spectrometer with preprogrammed multicomponent identification capability for ambient air monitoring and with space for 10 user-defined standards for calibration, AC/DC converter, sample probe, and carrying case costs $20,000
Industrial FTIR costs $75,000–$125,000

Partial list of suppliers

ABB Process Analytics—Bomem http://new.abb.com/products/measurement-products/analytical
Ametek http://www.ametekpi.com/products/Thermox-WDG-V-Combustion-Analyzer.aspx
Aqua Measure http://www.aquameasure.com/methods.htm
CAI http://www.gasanalyzers.com/products-ia.php
Combustion http://www.cambustion.com/products/ndir500/operating-principle
Control Instruments Corp. http://www.controlinstruments.com/technologies/infrared-analyzers
Enviro-Analytical http://www.enviro-analytical.com/enviroproducts/ftir_analyzers.html
Fuji Electric http://www.fujielectric.com/products/instruments/library/catalog/box/doc/ECNO325c.pdf
Horiba Instruments http://www.horiba.com/us/en/automotive-test-systems/products/emission-measurement-systems/portable-emission-analyzers/details/mexa-584l-826/
Infrared Industries http://www.infraredindustries.com/product/ir-8400d-dual-stream-gas-analyzer/
International Sensor Technology http://www.intlsensor.com/pdf/products.pdf
K2BW http://www.k2bw.com/5_c_18.htm
Midac http://www.midac.com/i-series.html
Moisture Register Products, of Aqua Measure Instruments, http://www.aquameasure.com/
NDC http://www.ndc.com/en/Products/At-Line-Near-Infrared-Analyzers/InfraLab-Meat-Analyzer.aspx
Servomex http://www.servomex.com/servomex/web/web.nsf/en/servoflex-minimp-5200-multipurpose
Shimadzu (A, B) http://www.shimadzu.com/an/spectro/uv/uv1800/uv2.html
Siemens http://www.automation.siemens.com/mcms/sensor-systems/en/process-analytics/gas-analyzer-gas-analysis/extractive/ir-active-components/pages/ultramat-23.aspx
Signal Instruments, http://www.k2bw.com/418.htm
Teledyne http://www.teledyne-ai.com/products/7500.asp
Thermo Scientific http://www.thermoscientific.com/en/search-results.html?keyword=Fourier+Transform+Infrared+Spectroscopy+%28FTIR%29&countryCode=US&matchDim=Y
Unity Scientific, http://www.unityscientific.com/products/wet-chemistry/sample-preparation
Wilks-Spectro Scientific Co. http://www.wilksir.com/products/infraran-specific-vapor-analyzers.html
Yokogawa http://www.yokogawa.com/an/ir-gas/an-ir-gas-001en.htm
Zeltex Inc. http://www.zeltex.com/portable/101.pdf
Most popular: ABB, Servomex, and Siemens

Fiber-optics, sample systems, tools

Axiom, sample systems, fibers, both NIR and IR http://www.goaxiom.com/process_products_NIR-UV.html#process_nir_multiplexer
Dave Mayes, a developer of spectroscopic tools (http://www.dsquared-dev.com)
Equitech International Corp., fiber switches, fiber connections to the process, sampling systems http://www.equitechintl.com/Multiplexer.htm
Fiber Tech Optica, fiber optics only http://www.fibertech.com/enterprise/fiber-optic-services/
Optec http://www.optek.com/Product_Detail.asp?ProductID=26
Remspec Corp. Fiber Optics http://ir-fiber.com/
Solutions Plus, Inc., makers of traceable standards, a division of Ricca Chemical http://www.riccachemical.com/

NEAR INFRARED ANALYZERS

Process fluids

Gas, liquid, or solid, but mostly liquid and solid

Some applications (See Table 1.32b)

Active ingredient in drugs
Benzene in gasoline, 0.2%–1%
Boiling points of gasoline, 50°C–200°C (122°F–392°F)
Btu of natural gas (high pressure)
Caustic in water 0.1%–10%
Cetane of diesel fuel

(*Continued*)

	Molecular weight of small polymers Octanes of gasoline, 80–100 Octanes of components of gasoline, 60–120 Protein content of wheat p-Xylene concentration in mixture of aromatics
Operating pressure	150 PSI standard (10 bar) 1000 PSI special (70 bar)
Ambient temperature	–40°C to 50°C (–40°F to 120°F) is standard. (Note: Since the ambient temperature changes, it will affect the spectrometer and it will require temperature stabilization.)
Stream temperature	This restricts cell material only; normally one keeps the temperature constant.
Humidity limitations	None—NIRs, like IRs, should be purged; this eliminates the humidity problem.
Materials of construction	Cell bodies in all standard materials; windows can be quartz (most common), sapphire, and others
Cell path lengths	For liquids, 0.04–4 in. (1–100 mm); for gas, long (unless sample is at high pressure so cell length becomes too long to be practical)
Warm-up time	Manufacturers normally quote minutes—recommend overnight for best stability
Repeatability	±0.01% of full scale
Linearity	±0.5% of full scale
Inaccuracy	±1% of span (depends on how well the "modeling" has been done; can be much better)
Drift	±0.01% of full scale and the same for span per day
Costs	$80,000–$180,000, depending on number of streams, distance between the analyzer and sample, and sample preparation required. (How can these costs be justified by the user? At one installation, the analyzer is determining 25 properties every 45 s. It is also possible to look at several streams and still update the control system as often as needed. At another installation, the plant estimated that the analyzer saved $15 million the first year it was in service.)
Partial list of suppliers	ABB Process Analytics—Bomen http://new.abb.com/products/measurement-products/analytical Bran and Luebbe—Technicon http://www.ebay.com/itm/Bran-Luebbe-IA450-Technicon-TechniServ-NIR-/221349142772 Brimrose Corporation of America http://www.brimrose.com/products/nir_mir_spectrometers/sort_by_spectrometers.html Foss-NIR Systems http://www.foss.dk/ Guided Wave http://www.guided-wave.com/products/spectrometers.html Hamilton Sundstrand (AIT Division—Analect) http://www.spectroscopyonline.com/spectroscopy//product/productDetail.jsp?id=48253 Jasco Analytical Instruments http://www.jascoinc.com/products/spectroscopy/uv-visible-nir LTI http://www.LTIndustries.com Ocean Optics http://www.coleparmer.com/Product/Ocean_Optics_Chem_USB4_Visible_NIR_Spectrophotometer/WU-83500–10 Rosemount Analytical, Inc.—Emerson http://www2.emersonprocess.com/siteadmincenter/PM%20Rosemount%20Analytical%20Documents/PGA_Manual_AOTF-NIR_200010.pdf Thermo Electron http://www.thermo.com/eThermo/CMA/PDFs/Various/File_27448.pdf Unity Scientific http://www.unityscientific.com/products/NIR/at-line/smartsampler.asp

INTRODUCTION

In the first part of this chapter, the infrared (IR) analyzers will be discussed, while the near-infrared (NIR) analyzers will be described in the second part of this chapter. This is not the only chapter where IR and NIR analyzers are discussed. As can be seen from the analyzer selection guide provided in Table 1.1a, IR and NIR analyzers are applicable to a wide range of analytical tasks.

It should also be noted that the boundaries between ultraviolet (UV), visible, NIR, and IR are slowly disappearing. Analyzers are evolving that are capable of operating in all of these spectra, and as the mathematical tools to handle full spectral ranges are becoming available. The addition of microprocessors or tabletop computers has enhanced the performance of these instruments by providing such features as self-calibration, self-diagnostics, and chemometric tools, for example, partial least squares (PLS) and principal

component regression (PCR), to name two, while design modularity has contributed to simplifying maintenance.

For an overall view of where process analysis is going, the annual conference of the International Forum for Process Analytical Chemistry (IFPAC) can be recommended. It is held annually and normally contains sessions on process IR and NIR; for more information, see http://www.ifpac.com.

PRINCIPLES OF ANALYSIS

The composition of both gases and liquids can be analyzed by measuring their absorption or reflectance in the infrared (IR) or near-infrared (NIR) spectral regions. These analyzers can operate either in the photometric (absorption) or in the spectrophotometric (dispersion) mode, and some designs are capable to operate in both.

IR absorption (or reflection used with solid samples) is a technique that can be used successfully for continuous chemical analysis. The infrared region of the electromagnetic spectrum is generally considered to cover wavelengths from 0.8 to 20,000 μm. NIR normally covers 0.8 to 2500 μm, and classic IR covers the rest. For IR analysis, these limits are normally put in terms of frequency (cm^{-1}, wave numbers or the number of waves per cm): 4000–500 cm^{-1}, which corresponds to wavelengths of 2,500–20,000 μm.

Except for a small overlap region, sources and detectors that are needed in the NIR will not work in the IR, and vice versa. Some laboratory spectrometers have both sources and detectors so they can work in both areas. For the process, most gas analysis is done in the IR and most solid and liquid analysis is done in the NIR. The choice is based on workable path lengths.

Infrared radiation interacts with almost all molecules (except the homonuclear diatomics oxygen (O_2); nitrogen (N_2); hydrogen (H_2); chlorine (Cl_2); etc., and monatomics such as helium (He); neon (Ne); etc.) by exciting molecular vibrations and rotations that affect the dipole of the molecule (Figure 1.32a). The oscillating electric field of the IR wave interacts with the electric dipole of the molecule, and when the IR frequency matches the natural frequency of the molecule, some of the IR power is absorbed.

The pattern of wavelengths, or frequencies, absorbed identifies the molecule in the sample. The strength of absorption at particular frequencies is a measure of the concentration of the species. Analytical laboratory IR is largely concerned with identification, or qualitative analysis, while process IR is concerned with quantitative analysis. Some typical spectra are shown in Figure 1.32b. The NIR consists of overtones and combinations of these IR bands.

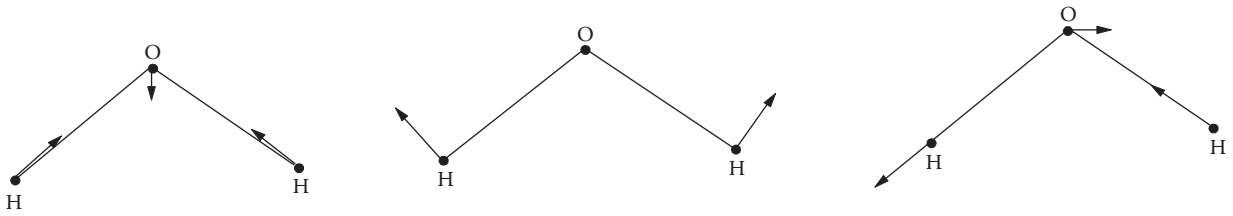
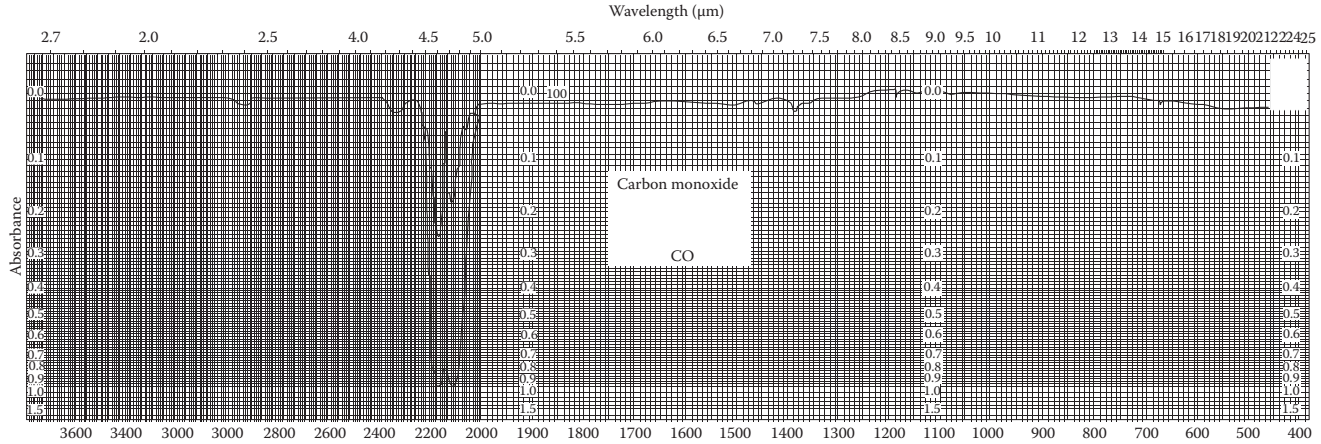


FIG. 1.32a

The three fundamental vibrations of the water molecule (left to right) are symmetric stretch, bend, and asymmetric stretch. The amplitudes of the vibrations have been exaggerated for clarity.



400 torr of CO of total 600. A distomic has only one fundamental absorbtion band. Higher resolution shows the band to consist of many sharp lines about 4 cm^{-1} aprt (rotational line structure).

FIG. 1.32b

Examples of IR spectra recorded using a laboratory double-beam spectrometer. All spectra are gas phase using a 2 in. (5-cm) cell with N_2 added to give a total pressure of 600 mmHg (torr). (Courtesy of Dow Chemical Co.) (*Continued*)

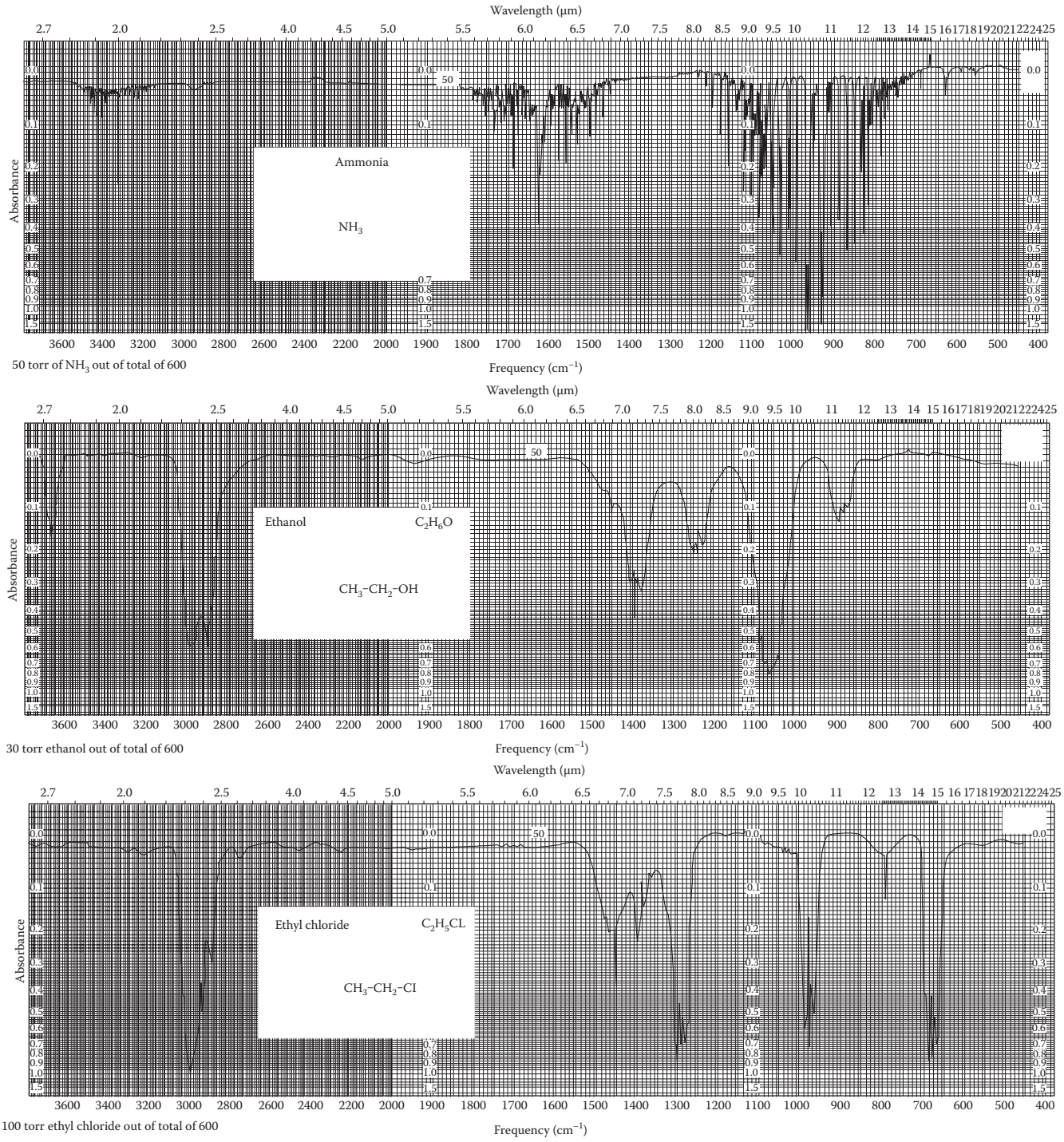


FIG. 1.32b (Continued)

Examples of IR spectra recorded using a laboratory double-beam spectrometer. All spectra are gas phase using a 2 in. (5-cm) cell with N_2 added to give a total pressure of 600 mmHg (torr). (Courtesy of Dow Chemical Co.)

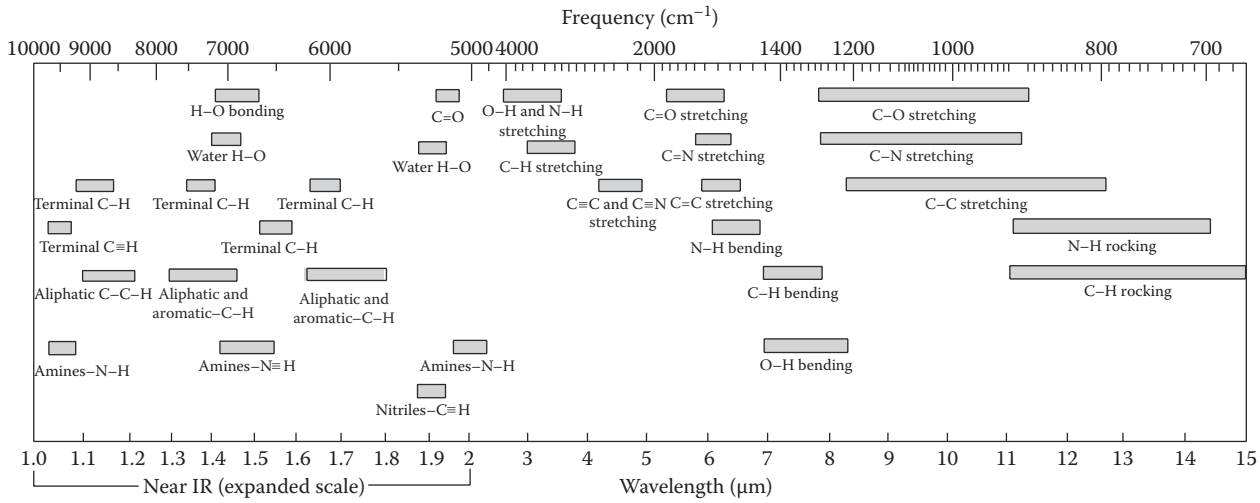


FIG. 1.32c
Functional group frequency chart. Fundamental vibrations absorb in the mid-IR; overtones and combination bond are 10–10,000 weaker and absorb in the NIR.

Particular groups of atoms tend to absorb at the same frequency with very little influence from the rest of the molecule. These group frequencies are a great help in identifying the molecules from the IR spectra (Figure 1.32c). On the other hand, similar molecules, such as a series of homologous hydrocarbons, have very similar IR spectra.

Infrared analysis is, therefore, most straightforward when the component molecules of the sample have significantly different atomic groupings. A mixture of aliphatic hydrocarbons would be better analyzed by another technique, such as gas chromatography. The part of the spectrum offering the best discrimination between molecules is between 7 and 15 μm, 1430 and 670 cm^{-1}, the so-called fingerprint region. Given the very large signal-to-noise ratio in the NIR, one can make very fine separations between similar species; for example, o-xylene can be measured in a mixture of xylene, ethylbenzene, and benzene.

Beer–Lambert Law

The starting point for quantitative analysis is the Beer–Lambert law, frequently just called Beer's law, which relates the amount of light absorbed to the sample's concentration and path length.

$$A = abc = \log_{10} \frac{I_0}{I} \qquad \textbf{1.32(1)}$$

where

A is the absorbance
I is the IR power-reaching detector with sample in the beam path
I_0 is the IR power-reaching detector with no sample in the beam path
a is the absorption coefficient of pure component of interest at analytical wavelength; the units depend on those chosen for b and c; a newer term, ε, extinction coefficient, is the preferred term in the academic literature
b is the sample path length, sometimes l is used
c is the concentration of sample component

The law states that concentration is directly proportional to absorbance at a given wavelength and path length at specified temperature and pressure. Note that, however, the logarithm